

Chapter one Transition element

	IA 1		Т	he	N	loc	ler	n I	Pel	rio	dia							18 Zero
1	Н	2											13	14	15	16	17	He
*	Mydragen	IIA		Table IIIA IVA						IVA	VA	VIA	VIIA	Phyliade health fam				
2	3	4					ak	JIC					5	6	7	8	9	10
2	Li	Be					-141-						В	C	N	0	F	Ne
	11	12		I	<i>r</i> iain	tran	SITIO	naie	elem	ents			13	14	15	16	17	18
3	Na	Mg	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIII	10	11 IB	12 IIB	Al	Si	P	S	CI	Ar
	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
4	K	Ca	Sc	Ti	٧	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	Phintings (that have	Californ Made April Street	Scartillan Sector Into	Thereps became home	Verelier Sections	Chartery haster floor	Managarinea Seattle-box	Sept man	Court	Nesei	Cooper	Time .	Golfam Nor hostin-Mai	Semention	Argenta market	Basesare Surger	Bratta	Morphon totals has
5	Rb	38	39 Y	Zr	Nb	42 NAO	43 To	44 D.	Rh	46 Del	47	Cd	49	50	Sb	Te	53	Xe
)	Battle	Sr	Total	ZI	IND	Мо	To	Ru	Platie	Pd	Ag	Catrium	In	Sn	SD	Tellmen	1000	Notes
	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
5	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
	Contain statem	Barton Deliveration	Lanthamuri. Horacox	Hartstam Translate Blood	Tortular Securities	Tungates Terestor-tros	Riveriam Territor from	Dominal Terrorie Mass	Milian Textorine	Fletnum. Investor-mod	God Coasse too	Manney	Distillate has been deter-	Load Net Tourist had	Blamath her tonsine man	Polanium Interior	Astalite	Radon feets line
7	87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
1	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	FI	Mc	Lv	Ts	Og
	tool term	Name and Street	4000	house tes	tentered	Sauto Sea	7	he In	ner T	rans	ition	Flem	ents	Transfer Street	THE SAME THE	No hadronista	*Sheet	Jugat dans
					58	59	60	61	62	63	64	65	66	67	68	69	70	71
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu		
		211			Cartists	Present/mium	Naceproper serveres	Proposition	Sanurain.	Surregion	Caterious	Tortision Lacronica	Dyspressive	Habelum	Inter	Tholian	Thartien	Luterium
					90	91	92	93	94	95	96	97	98	99	100	101	102	103
Actinides Th Pa U			ctini	des	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Economic importance:

- **1 Scandium:** It is found in very small amount spread on a large area in the earth's crust. On adding a little amount of scandium to aluminum it gives light and very hard alloy used in manufacture of Mirage fighter also it is added to Mercury vapour lamps to produce light with high quality looks like sun light, so it is used in TV Photography at night.
- **2 Titanium :** Strong element of rigidity as steel ,but it is less denser than steel, its alloys are used in the manufacture of aircraft and space shuttle because it maintains its durability at high temperatures while the hardness of aluminum decrease, it is used in the dental implants and Industrial joints because,the body does not eject it and does not cause any type of poisoning from the famous Titanium compound Titanium dioxide (TiO₂) that is used in Sun protection cosmetics, where minute nanoparticles prevent effect of the UV on the skin.
- **3 Vanadium:** when we add a small portion of it to the steel a high hardness alloy is formed and has great ability to resist corrosion so it is used in the manufacture of car springs. The important compounds of vanadium: Vanadium penta oxide is used in manufacture of dyes used in ceramics and glass industry; also it is used as a catalyst and manufacture of strong magnetic conductors.

- **4 Chromium :** It is chemically active metal but it resist the effect of the atmospheric air due to the formation of a metal oxide on its surface , in which the molecular volume of the produced oxide is larger than that of the metal which forms a nonporous layer of metal oxide that prevent the continued interaction with oxygen of air, Chromium is used in metal plating and leather tanning. The important compounds of chromium: Chromium III oxide Cr_2O_3 that used in manufacture of dyes and potassium dichromate($K_2Cr_2O_7$) that used as oxidizing agent.
- **5 Manganese :** Manganese is not used as a pure metal because it is brittle metal so always used as alloys or compounds. Ferromanganese alloy is used in railway track, because it is harder than steel, aluminum and manganese alloys are used in manufacture of Soft drinks vessels (cans) because it resists corrosion. The important compounds of manganese: Manganese dioxide MnO_2 which acts as strong oxidizing agent used in dry cell, potassium permanganate $KMnO_4$ that used as antiseptic substance and manganese II sulphate K_2SO_4 that used as a fungicide.
- **6 Iron:** Used in manufacture of concrete, electricity pylons, knifes, gun and cannons pipes and surgical instruments. Also used as a catalyst in the manufacture of ammonia by Haber-Bosch method and the conversion of water gas (mixture of hydrogen and carbon monoxide) to a fuel by Fischer-Tropsch method.
- **7 Cobalt :** It is similar to iron in which both of them can be magnetized so they are used in the manufacture of magnets. Cobalt is used in manufacture of modern dry batteries that used in cars. Cobalt has twelve radioactive isotopes, cobalt 60 is very important one because it produces gamma rays which have high penetrating power so it is used preserving food, in industry used for the detection about the quality of the industrial products, whereas it detects about welding cracks, links sites and in medicine used for detecting and treating tumors.

8 - Nickel:

It is used in the manufacture of nickel – cadmium battery which can be recharged. It forms with steel alloys which are hard and resist rust and the effect of acids. Nickel chromium alloys are used in heaters and electric furnaces coils because they resist corrosion at high temperature, nickel is used for panting the other metals to protect them from oxidation and rust and give these metals beautiful appearance. Finally divided nickel is used as a catalyst like in hydrogenation processes of oil.

- **9 Copper :** Copper is the first discovered metal, copper ten alloys are known as bronze alloy. Copper is good conductor of electricity so it is used in electric cables and coins industry, copper II sulphate CuSO₄ is used as insecticide and fungicide in the purification of water. Fehling solution (one of copper compounds)**is** used to detect glucose in which its blue colour changes to orange.
- **10 Zinc:** It is used in the galvanizing other metals to protect them from rusting. Zinc oxide ZnO is used in the manufacture of paints, rubber and cosmetic materials, zinc sulphide ZnS is used in manufacture of lighted paints (coatings) and x-ray screens.

The Electronic Configurations and Oxidation states:

The	The	The electron	oxidation	Some of the compounds
element	group	configuration	states	
₂₁ Sc	IIIB	$[Ar], 4s^2, 3d^1$	3	Sc_2O_3
₂₂ Ti	IVB	$[Ar],4s^2,3d^2$	2 ,3 ,4	TiO ₂ , Ti ₂ O ₃ , TiO
23V	VB	$[Ar],4s^2,3d^3$	2, 3, 4, <u>5</u>	V_2O_5 , VO_2 , V_2O_3 , VO
₂₄ Cr	VIB	[Ar],4s ¹ ,3d ⁵	2 ,3 ,6	CrO ₃ , Cr ₂ O ₃ , CrO
₂₅ Mn	VIIB	$[Ar], 4s^2, 3d^5$	2, 3, <u>4</u> , 6, 7	MnO ₂ , Mn ₂ O ₃ , MnO
				KMnO ₄ , K ₂ MnO ₄
₂₆ Fe	VIII	$[Ar],4s^2,3d^6$	2, 3, 6	Na ₂ FeO ₄ , Fe ₂ O ₃ , FeO
₂₇ Co	VIII	$[Ar],4s^2,3d^7$	2, <u>3</u> , 4	, CoCl ₃ , CoCl ₂
₂₈ Ni	VIII	$[Ar],4s^2,3d^8$	<u>2</u> , 3, 4	NiO ₂ ,Ni ₂ O ₃ ,NiO
₂₉ Cu	IB	$[Ar],4s^1,3d^{10}$	1, <u>2</u>	CuO ,Cu ₂ O
₃₀ Zn	IIB	$[Ar],4s^2,3d^{10}$	2	ZnO

show the colours of some hydrated ions of the metals of the first transition series.

No. of electrons in	The colour	No. of electrons in 3d	The colour
3d of the ion		of the ion	
$Sc^{+3}_{(aq)}$ (3d ⁰)	colourless	$Fe^{+3}_{(aq)} \qquad (3d^5)$	Yellow
$Ti^{+3}_{(aq)}$ (3d ¹)	red purple	$Fe^{+2}_{(aq)} \qquad (3d^6)$	Green
$V^{+3}_{(aq)}$ (3d ²)	Blue	$Co^{+2}_{(aq)} \qquad (3d^7)$	Red
$Cr^{+3}_{(aq)}$ (3d ³)	Green	Ni ⁺² _(aq) (3d ⁸)	Green
$Mn^{+3}_{(aq)}$ (3d ⁴)	Violet	$Cu^{+2}_{(aq)} \qquad (3d^9)$	Blue
$Mn^{+2}_{(aq)}$ (3d ⁵)	Red (pink)	Zn ⁺² _(aq) (3d ¹⁰)	colourless

The general properties of the first transition elements :

	The	The	The	The	The boiling
The element	atomic	atomic	density	melting	point ⁰ C
	mass	radius	g/cm ³	point ⁰ C	
Scandium Sc	45	1.44	3.10	1397	3900
Titanium Ti	47.9	1.32	4.42	1680	3130
Vanadium V	51	1.22	6.07	1710	3530
Chromium Cr	52	1.17	7.19	1890	2480
Manganese Mn	54.9	1.17	7.21	1247	2087
Iron Fe	55.9	1.16	7.87	1528	2800
Cobalt Co	58.9	1.16	8.70	1490	3520
Nickel Ni	58.7	1.15	8.90	1492	2800
Copper Cu	63.5	1.17	8.92	1083	2582

Extraction of Iron from the Ores

1- Improving the physical and mechanical properties of iron:

Crushing processes: The obtain the ore in suitable size to be easily reduced.

<u>Sintering processes:</u> The process of treating fine particles of iron ores to obtain large particles.

<u>Concentrating process</u>: This process is used to removes most of the impurities which are chemically combined or mixed with the ore, this is formed by using the surface tension or magnetic or electric the obtain the ore in suitable size to be easily reduce

2-Improving the chemical properties: Roasting

a) Drying the ore and expelling humidity, to increase the percentage of iron in the ore.

2 Fe₂O₃ .3H₂O_(s)
$$^{\prime}$$
(40%Fe) \longrightarrow **2**Fe₂O_{3(s)} $^{\prime}$ (69.6%Fe) + **3**H₂O_(y)

b) Oxidation of some impurities such as sulphur and phosphorus.

$$\begin{array}{ccc} S_{(s)} & + & O_{2(g)} & & & \longrightarrow & SO_{2(g)} \\ 4P_{(s)} + 5O_{2(g)} & & & \longrightarrow & 2P_2O_{5(g)} \end{array}$$

Types of alloys:

1-Interstitial alloys:

Pure iron, as other metals, is formed of a Crystal lattice of metal atoms are arranged in compact closed rows. On hammering, a layer of metal atoms Can slip one over the other.

However the introduce an element with small atomic size to another pure metal in the Intermolecular spaces of the crystal lattice of the main element this prevent the movement of the metal layers this will increase the hardness of the metal and change the physical properties of the metal like malleability, ductility, melting point, electric conductivity and magnetic properties of metal. Such as iron and carbon alloy (Steel).

2-Substitution alloys:

In this type of alloys some of the atoms of the pure metal are replaced by atoms of other metal which having the same atomic radius ,crystal lattice and the chemical properties such as(Ferrochrome alloy) in the stainless steel, (copper- gold alloy) and (ferronickel alloy).

3) Inter-metallic alloys:

In this type of alloys the elements forming the alloy combine with each other chemically to form chemical compound. its formula disobey valence law, and the compounds formed are solids consists of metals are not in the same group in the periodic table, such as Aluminum –Nickel alloy(Ni₃Al) which is called Dure alumin and lead – gold alloy (Au₂Pb) and cementite (Fe₃C)

Iron reactions:

a) Drying the ore and expelling humidity, to increase the percentage of iron in the ore.

FeCO₃₍₃₎
$$\xrightarrow{\triangle}$$
 FeO₍₄₎ + CO_{2(g)}
48.5% iron
2FeO₍₄₎ + ½ O_{2(g)} $\xrightarrow{\triangle}$ Fe₂O_{3(3)(69.6%Fe)}
2Fe₂O₃ $3H_2O_{13}^{\dagger}$ (4078Fe) $\xrightarrow{\triangle}$ 2Fe₂O_{3(3)(69.6%Fe)} +3H₂O₍₄₎

b) Oxidation of some impurities such as sulphur and phosphorus.

$$S_{(s)} + O_{2_{(g)}} \xrightarrow{\Delta} SO_{2_{(g)}}$$

$$4P_{(s)} + 5O_{2_{(g)}} \xrightarrow{\Delta} 2P_2O_{5_{(g)}}$$

Second: Reduction of Iron Ores

a) Reduction, by carbon monoxide resulting from coke in the blast furnace.

b) Reduction by a mixture of carbon monoxide and hydrogen (water gas)resulting from natural gas (93% methane) in the midrex furnace.

Iron properties:

1. Effect of air:

$$3Fe_{(a)} + 2O_{2_{(a)}} \xrightarrow{\Delta} Fe_3O_{4_{(a)}}$$

2. Effect of water:

$$3Fe_{(a)} + 4H_2O_{(a)} \xrightarrow{500^{\circ}C} Fe_3O_{4_{(a)}} + 4H_{2_{(a)}}$$

3. with non-metals:

$$2Fe_{(a)} + 3Cl_{2_{(a)}} \xrightarrow{\Delta} 2FeCl_{3_{(a)}}$$

$$Fe_{(a)} + S \xrightarrow{\Delta} FeS_{(a)}$$

$$\frac{\text{4. with Acids:}}{\text{Fe}_{\text{(a)}} + \text{H}_2\text{SO}_{4_{\text{(a)}}} \longrightarrow \text{FeSO}_{4_{\text{(a)}}} + \text{H}_{2_{\text{(a)}}}$$

$$Fe + 2HCl_{(aq)} \xrightarrow{dil.} FeCl_{2(aq)} H_{2_{(aq)}}$$

$$3Fe_{(a)} + 8H_2SO_{4_{(a)}} \xrightarrow{Conc} FeSO_{4_{(a)}} + Fe_2(SO_4)_{3_{(a)}} + 4SO_2 + 8H_2O_{(a)}$$

Iron Oxides:

1-Iron (II) Oxide Fe O:.

Preparation:

COO
$$| \xrightarrow{/} \text{Fe} \xrightarrow{\Delta} \text{in abcence of air} \rightarrow \text{FeO+CO+CO}_{2}$$
COC
$$| \text{(s)} \text{(g)} \text{(g)}$$

$$| \text{Fe}_{2}\text{O}_{3} + \text{H}_{3} \xrightarrow{400-700^{\circ}\text{C}} \rightarrow 2 \text{ FeO} + \text{H}_{2}\text{O}$$

Properties:

$$Fe_3O_4 + H_2 \xrightarrow{400-700^{\circ}C} 3 FeO + H_2O$$

$$4 \text{ FeO} + O_2 \xrightarrow{\Delta} 2 \text{ Fe}_2 O_3$$

$$\label{eq:FeO+H2SO4} \begin{split} \text{FeO+H}_2\text{SO}_4 &\xrightarrow{\text{(dil.)}} \text{FeSO}_4 \\ \text{(s)} &\text{(aq)} &\text{(aq)} &\text{(l)} \end{split}$$

2- Iron (III)oxide Fe₂O₃:

Preparation:

$$FeCl3+3NH4OH \rightarrow Fe(OH)3 \downarrow +3NH4Cl$$

$$2Fe(OH)3 \xrightarrow{above} Fe2O3+3H2O$$

$$2 \text{ FeSO}_4 \xrightarrow{\Delta} \text{Fe}_2 \text{O}_3 + \text{SO}_2 + \text{SO}_3$$

Properties:

$$Fe_2O_3 + 3H_2SO_4 \xrightarrow{\Delta} Fe_2(SO_4)_3 + 3H_2O$$

3- The black oxide (magnetic iron oxide) Fe₃O₄:

Preparation:

$$3\text{Fe}_2\text{O}_3 + \text{CO} \xrightarrow{230-300^\circ\text{c}} 2\text{F}_3\text{O}_4 + \text{CO}_2$$

Properties:

$$Fe_3O_4 + 4H_2SO_4 \xrightarrow{conc.} FeSO_4 + Fe_2(SO_4)_3 + 4H_2O$$

$$2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 \xrightarrow{\Delta} 3\text{Fe}_2\text{O}_3$$

Chapter two Chemical analysis

Mole: Quantity of substance which contains Avogadro's number of particles

(Molecules or atoms or ions or formula units or electrons)

$$Al^{3+} + 3e^{-} \rightarrow Al$$

- *Molar mass (g) = The sum of atomic masses of the elements forming the molecule in gram
- *Number of moles (mol) = mass of substance (g) / Molar mass (g/mol)
- *Number of molecules (or atoms or ions) = number of moles of molecules Avogadro's number (6.02×10^{23})
- *volume of gas (L) = number of molar gas (mol) x 22.4 (L/mol) at STP
- * Density of gas (g/L) = molar mass (g/mol) / 22.4 (L/mol) at STP
- *molar concentration (M) = number of moles (mol) / volume of solution (L)
- *the mass percentage of an element in compound (g/g%) =

Mass of element in one mole of compound x100 / molar mass of the compound

*the mass percentage of compound in impure sample =

Mass of compound in sample x100 / mass of impure sample

Kind of chemical analysis:

1-Qualitative analysis:

It involves the identification of the constituents of a compound wether it is a sample salt of mixtures of several compounds

2-Quantitative analysis:

It involves the calculation of the percentage of each component in a compound include the identification of <u>acid radical (anions) of salts and basic radical (cations)</u> of salts

A-Identification of the Acidic radicals (anions):

1- Anions of Hydrochloric acid group

The main experiment: solid salt + Dilute Hydrochloric acid

Anion	Symbol	Gas liberated and Its detection	Confirmatory test for anion
(1) carbonate	(CO ₃) ²⁻	Na ₂ CO _{3(s)} + 2HCl _(aq) → 2NaCl _(aq) + H ₂ O _(f) + CO _{2(g)} Effervescence tacks place and CO ₂ gas evolved which turn clear lime water milky CO _{2 (g)} + Ca(OH) _{2(aq)} S.T. CaCO _{3(s)} + H ₂ O _(j)	Salt solution + magnesium sulphate solution .a white ppt. is formed on cold soluble in hydrochloric acid. Na ₂ CO _{3(aq)} + MgSO _{4(aq)} Na ₂ SO _{4(aq)} + MgCO _{3(a)} + MgCO _{3(a)} + 2HCl _(aq) -> MgCl _{2(aq)} + H ₂ O _(i) + CO _{2 (g)}

		CO ₂ is passed for short time to avoid conversion of calcium carbonate to calcium bicarbonate so ppt. will disappear	Note all metal carbonates are water insoluble except sodium potassium and, ammonium carbonate and all carbonates are soluble in acids .
(2) Bicarbonate	(HCO ₃) ¹ ·	NaHCO _{3(s)} + HCl _(sq) -> NaCl _(sq) + H ₂ O _(f) + CO _{2(g)} Effervescence tacks place and CO ₂ gas evolved which turn clear lime water milky Note all bicarbonates are soluble in water	Salt solution + magnesium sulphate solution . a white ppt. is formed after heat 2 NaHCO _{3(aq)} + MgSO _{4(aq)} → Na ₂ SO _{4(aq)} + Mg(HCO ₃) _{2(aq)} Mg(HCO ₃) _{2(aq)} △ → MgCO _{3(a)} + CO _{2(g)} + H ₂ O _(j)
(3) Sulphite	(SO ₃) ² ·	Na ₂ SO _{3(a)} + 2HCl _(aq) → 2NaCl _(aq) +H ₂ O _(l) + SO _{2(g)} Sulphur dioxide gas evolved which has a very Irritating smell and turns a paper wet with potassium dichromate acidified by sulphuric acid to green	Salt solution + silver nitrate solution white ppt. is formed which turn black by heat Na ₂ SO _{3(sq)} +2 AgNO _{3(sq)} →Ag ₂ SO _{3(s)} +2NaNO _{3(sq)}

		$K_2Cr_2O_{7(aq)} + 3SO_{2(g)} + H_2SO_{4(aq)} \longrightarrow K_2SO_{4(aq)} + Cr_2(SO_4)_{3(aq)} + H_2O_{(1)}$	
(4) Sulphide	S ² -	Na ₂ S _(s) + 2HCl _(sq) → 2NaCl _(aq) + H ₂ S _(g) Hydrogen sulphide gas evolved which Has bade Smell, turns a paper wet with lead acetate to black (CH ₃ COO) ₂ Pb _(aq) + H ₂ S _(g) →PbS _(s) + 2CH ₃ COOH _(aq)	Salt solution + silver nitrate solution black ppt. is formed from silver sulphide Na ₂ S (aq) +2 AgNO _{3(aq)} → Ag ₂ S (s)+ 2NaNO _{3(aq)}
(5) thiosulphate	(S ₂ O ₃) ² ·	Na ₂ S ₂ O _{3(s)} + 2HCl _(aq) → 2NaCl _(aq) +H ₂ O _(l) + SO _{2(g)} + S _(s) Sulphur dioxide gas evolved and yellow ppt. as a result of suspend sulphur in solution	Salt solution + iodine solution → the brown colour of iodine is removed $2 \text{ Na}_2 \text{S}_2 \text{O}_{3(\text{nq})} + \text{I}_{2 (\text{nq})} \longrightarrow$ $\text{Na}_2 \text{S}_4 \text{O}_{6(\text{nq})} + 2 \text{NaI}$ (sodium Tetra thionate)
(6) Nitrite	(NO ₂)	$NaNO_{2(s)} + HCI_{(aq)} \longrightarrow$ $NaCI_{(aq)} + HNO_{2(aq)}$ $3HNO_{2(aq)} \longrightarrow HNO_{3(aq)}$ $+ H_2O_{(1)} + 2NO_{(g)}$	Salt solution + potassium permanganate acidified by conc. sulphuric acid The violet colour of permanganate is removed
		Colourless nitric oxide gas	5NaNO _{2(aq)} + 2KMnO _{4(aq)} +

Colourless nitric oxide gas	5NaNO _{2(aq)} + 2KMnO _{4(aq)} +
evolved which turned	3H ₂ SO _{4(aq)} →
reddish brown at the	5NaNO _{3(aq)} + K ₂ SO _{4(aq)} +
mouth of the tube	$2MnSO_{4(aq)} + 3H_2O_{(1)}$
$2NO_{(g)} + O_2 \longrightarrow 2NO_{2(g)}$	200-03 200-000

(2) Concentrated sulphuric acid group

The main experiment:

Add concentrated sulphuric acid to the solid salt and heat if necessary.

Anions	Gas liberated	Confirmatory tests
Chloride (Cl')	HCl gas is evolved, which is colourless . it gives white fumes with glass rod wet with ammonia solution. 2 NaCl _(s) + H ₂ SO _{4(L)} conc./△> Na ₂ SO _{4(aq)} + 2HCl _(g) HCl _(g) + NH _{3(g)} → NH ₄ Cl _(s)	Salt solution + silver nitrate solution white ppt. is formed from silver chloride which turns violet in sun light, soluble in conc. ammonia solution NaCl (aq) + AgNO _{3(aq)} > AgCl (s)+ 2NaNO _{3(aq)}

Bromide (Br)	HBr gas is evolved, which is colourless . it partially oxidized by sulphuric acid and orange red fumes from bromine will be separated turns a paper wet by starch yellow. 2NaBr _(s) + H ₂ SO _{4 (l)} conc./Δ Na ₂ SO _{4(sq)} + 2HBr _(g) 2HBr _(g) + H ₂ SO _{4 (l)} →2H ₂ O _(l) + SO _{2(g)} + Br _{2(v)}	Salt solution + silver nitrate solution white-yellow ppt. is formed from silver bromide which turns dark in sun light , soluble slowly in conc. ammonia NaBr _(aq) + AgNO _{3(aq)} \longrightarrow AgBr _(s) + NaNO _{3(sq)}
Iodide (I')	HI gas is evolved, which is colourless. it partially oxidized quickly by sulphuric acid and violet fumes from iodine will be separated after heat turns a paper wet by starch blue.	Salt solution + silver nitrate solution yellow ppt. is formed from silver iodide insoluble in ammonia solution NaI (aq) + AgNO _{3(aq)} >
	$2KI_{(s)} + H_2SO_{4(l)}$ conc./ Δ $K_2SO_{4(nq)} + 2HI_{(g)}$ $2HI_{(g)} + H_2SO_{4(l)}$ conc. $\Rightarrow 2H_2O_{(l)} + SO_{2(g)}$ $+ I_{2(v)}$	AgI (s)+ NaNO _{3(sq)}
Nitrate (NO ₃)	Brown vapour of nitrogen dioxide evolves due to the decomposition of the HNO ₃ The density of vapour increased by	The brown ring test. Nitrate salt solution + freshly prepared solution of iron II sulphate + few drops of conc. H ₂ SO ₄ are carefully added on

2NaNO _{3(s)} + H ₂ SO _{4(l} yconc_/Δ> Na ₂ SO _{4(sq)} + 2HNO _{3(l)} 4HNO _{3(l)} Δ 2H ₂ O _(l) + 4NO _{2(g)} + O _{2(g)} 4HNO _{3(l)} + Cuconc_/Δ> Cu(NO ₃) _{2(sq)} + 2H ₂ O _(l) +2NO _{2(g)}	inner surface of tube. A brown ring appears at the interface Of acid and reactant solutions Disappears by heat or shaking 2NaNO _{3(aq)} +6FeSO _{4(aq)} + 4H ₂ SO _{4 (l)} conc Na ₂ SO _{4(aq)} + + 3Fe ₂ (SO ₄) _{3(aq)} + 4H ₂ O _(l) + 2NO _(g) FeSO _{4(aq)} + NO _(g) FeSO ₄ .NO _(s) brown ring compound
---	---

Barium chloride solution group

(1)	Salt solution + barium chloride	Salt solution + silver nitrate
Phosphates	solution \rightarrow a white ppt. of	solution yellow ppt. is formed
$(PO_4)^{3-}$	barium phosphate soluble in	from silver phosphate soluble
	Dil HCl	in both ammonia solution and
	$2Na_3PO_{4(aq)} + 3 BaCl_{2 (aq)} \longrightarrow$	nitric acid
	$Ba_3(PO_4)_{2(s)} + 6NaCl_{(aq)}$	Na ₃ PO _{4(aq)} +3 AgNO _{3(aq)}
		\longrightarrow Ag ₃ PO _{4 (s)} +3 NaNO _{3(aq)}
(2) sulphate (SO ₄) ²⁻	Salt solution + barium chloride solution \rightarrow a white ppt. of barium sulphate insoluble in Dil HCl Na ₂ SO _{4(aq)} + BaCl _{2 (aq)} \rightarrow BaSO _{4 (s)} + 2NaCl (aq)	Salt solution + lead (II)acetate solution →a white ppt. of Lead(II) Sulphate Na ₂ SO _{4(aq)} + (CH ₃ COO) ₂ Pb _(aq) →2CH ₃ COONa (aq) + PbSO _{4(s)}

B- Identification of basic radical

the first analytical group which are chloride of

silver(I), mercury (I), lead (II) sparingly soluble in water so they can be precipitated using dil. Hydrochloric acid as reagent.

second analytical group:

cations of this group are precipitated in the form of sulphides in acidic medium , by dissolving the salt in water and adding dilute Hydrochloric acid to it to make solution acidic then passing hydrogen sulphide gas to it.**Cu**²⁺ is one from this group

Test for copper (II) cation Cu²⁺

Copper (II) salt solution + group reagent ($HCI + H_2S$) black ppt. from copper(II) sulphide is formed soluble in hot nitric acid

$$CuSO_{4(aq)} + H_2S_{(g)} \rightarrow H_2SO_{4(aq)} + CuS_{(s)}$$

third analytical group:

they are precipitated as hydroxides using ammonium hydroxide if they are not mixed with other cations .

cations to be studied: aluminium , iron(II) , iron(III)

<u>The main experiment:</u> salt solution + ammonium hydroxide (group reagent)

Cation	Reaction with group reagent	Confirmatory test
Aluminium Al ³⁺	Al ₂ (SO ₄) _{3 (aq)} + 6NH ₄ OH _(aq) → 3(NH ₄) ₂ SO _{4(aq)} +2Al(OH) _{3(a)} White gelatinous ppt. of Aluminium hydroxide soluble In dil. Acids and in caustic soda	Salt solution + sodium hydroxide solution White gelatinous ppt. of Aluminium hydroxide soluble in excess sodium hydroxide forming sodium meta aluminate Al ₂ (SO ₄) _{3 (aq)} + 6NaOH _(aq) → 3Na ₂ SO _{4(aq)} +2Al(OH) _{3(s)} Al(OH) _{3(s)} + NaOH _(aq) → NaAlO _{2 (aq)} + 2H ₂ O _(l)
Iron (II) Fe ²⁺	FeSO _{4 (aq)} + 2NH ₄ OH _(aq) → (NH ₄) ₂ SO _{4(aq)} +Fe(OH) _{2(s)} White ppt. turns white green When it exposed to air and soluble in acids	Salt solution + sodium hydroxide solution White green ppt. of iron(II)hydroxide is formed FeSO _{4 (aq)} + 2NaOH _(aq) → Na ₂ SO _{4(aq)} +Fe(OH) _{2(s)}

Iron (III) Fe ³⁺	FeCl ₃ +3 NH ₄ OH _(aq) → 3NH ₄ Cl + Fe(OH) _{3(a)} Reddish brown gelatinous ppt. Soluble in acids	Salt solution + sodium hydroxide solution Reddish brown ppt. of iron(III)hydroxide is formed FeCl _{3 (aq)} + 3NaOH _(aq) → 3 NaCl _(aq) +Fe(OH) _{3(a)}
--------------------------------	---	--

Fifth Analytical group

The main experiment: salt solution + ammonium carbonate solution (group reagent)

Cation	Reaction with group reagent	Confirmatory tests
		1)
Calcium	$CaCl_{2(aq)} + (NH_4)_2CO_{3(aq)} \rightarrow$	Salt solution + dil. Sulphuric acid
Ca ²⁺	2NH ₄ Cl _(aq) + CaCO _{3(S)}	A white ppt. of calcium sulphate
	a white ppt. of calcium	Is formed
	carbonate soluble in dil. HCl	$CaCl_{2(aq)} + H_2SO_{4(aq)} \rightarrow$
	and also in water containing CO2	2HCl _(aq) + CaSO _{4(s)}
	$CaCO_{3(s)} + H_2O_{(l)} + CO_{2(g)} \rightarrow$	ANSWER TESSARY
	Ca(HCO ₃) _{2(aq)}	
		2) flame test:
		Volatile calcium cation gives
		bunsen flam a brick red colour

The following table shows some indicators used in the neutralization reactions

Indicator	Colour in acidic medium	Colour in basic medium	Colour in neutral medium
Methyl orange	Red	Yellow	Orange
Phenolphthalein	Colourless	Red	colourless
Litmus	Red	Blue	purple
Bromothymol blue	Yellow	Blue	pale green

The laws of the chapter: The number of moles of added acid

The number of moles of added acid $\,=\,$ volume of solution in liter \times the concentration

One liter = 1000 ml.

You can simplify the calculation by substituting in the following mathematical equation:

$$Ma Va/n_a = Mb Vb/n_b$$

Where: M_a =concentration of the acid used (mole/liter).

V_a=volume of acid used (ml).

n_a= number of moles of the acid shown in the balanced chemical equation.

M_b=concentration of the alkali used(mole / liter).

V_b= volume of the alkali used (ml).

n_b=number of moles of alkali shown in the balanced chemical equation.

:. % Water of crystallization =
$$\frac{mass\ of\ water\ \times 100}{mass\ of\ hydrated\ sample}$$

(A)Volatilization method: This method is based on the volatilization of the element or compound to be determined followed by its measurement either by collecting the volatile material and determining its mass or by measuring the amount lost from the original mass of the substance.

(B) <u>Precipitation Method</u>: This method is based on precipitation of the analyte in the form of pure sparingly soluble compound with constant and known chemical structure. The precipitate is isolated from the solution by filtration on an ash less filter paper (a type of filter papers upon ignition leaves no ash).

Chapter3(Chemical equilibrium)

The equilibrium system: is apparently a stationary system but in reality dynamic.

Complete reactions"

In this type the reactions goes mostly in one direction (approximately forward).

Reversible reactions:

they are reactions in which both the reactants and products are always found in the reaction medium at equilibrium .

Chemical equilibrium in reversible reactions:

It is a dynamic system takes place when the rate of forward reaction equals the rate of backward reaction, and The concentrations of the reactants and products are not changed: The equilibrium position remains unchanged since all reactants and products are still found in the medium of reaction, (no gas evolves, no precipitate is formed) and as long as the reaction conditions such as temperature and pressure are not changed.

<u>The rate of a chemical reaction</u>: is measured by change in concentration of the reactants per unit time.

Factors affecting the rate (speed) of chemical reactions :-

1-Nature of the reactants. 2- Concentration of the reactants.

3- Reaction temperature. 4- Pressure.

5- Catalysts. 6- Light.

<u>Law of mass action</u>: - At a constant temperature, the rate of a chemical reaction is directly proportional to the result of multiplication of the reactant concentrations; each is raised to the power of the number of molecules or ions in the balanced chemical equation.

Calculation of equilibrium constant K_c:

At equilibrium: $r_1 = r_2$

$$k_1 [FeCl_3][NH_4SCN]^3 = k_2 [Fe(SCN)_3][NH_4Cl]^3$$

$$\frac{k_1}{k_2} = K_c = \frac{[Fe(SCN)_3] - [NH_4Cl]^3}{[FeCl_3] - [NH_4SCN]^3}$$

<u>Activation energy:</u> The minimum amount of energy that must be gained by a molecule to react at collision.

<u>Activated molecules:</u> Are those molecules which have kinetic energy that equals or exceeds the activation energy.

Calculation of equilibrium constant K_P:

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{\text{high pressure/cooling}} 2NH_{3(g)} \quad \text{, } \Delta H = -92Kj \quad \text{Kp = (P_{NH3})}^2 \text{/ (P_{N2}) X (P_{H2})}^3$$

*As in Kc the value of Kp for the reaction does not change by change partial pressure of reactant or product gases at same temperature and the total pressure of reaction is the summation of all partial pressure of gases (and depend on the number of moles for each gas)

Le Chatelier's principle :

The changes in any conditions of a system under equilibrium such as concentration, pressure or temperature the system activated to direction which decrease or cancels the effect of change.

Application of law of mass action in ionic equilibrium.

1 – Electrolytes Solutions: The following table represents the ionization constants of some weak acids:

Acid	Chemical formula	Ionization constant (ka)
Sulphurous acid	H ₂ SO ₃	1.7×10^{-2}
Hydrofluoric acid	HF	6.7 × 10 ⁻⁴
Nitrous acid	HNO ₂	5.1 × 10 ⁻⁴
Acetic acid	CH ₃ COOH	1.8×10^{-5}
Carbonic acid	H ₂ CO ₃	4.4 × 10 ⁻⁷
Boric acid	H ₃ BO ₃	5.8 × 10 ⁻¹⁰

Weak acids are arranged according to decreasing their strengths by significance of their ionization constant(K_a)

<u>Ionization:</u> a process in which unionized molecules are changed into ions.

<u>Complete Ionization:</u> a process in which all unionized molecules are changed into ions, and this happens in strong electrolytes.

<u>Incomplete (weak) Ionization:</u> a process in which a small part of unionized molecules are changed into ion, and this happens in weak electrolytes.

<u>lonic equilibrium:-</u> It is the equilibrium arising between molecules of a weak electrolyte and the ions resulting from it.

The law of mass action can not be applied in the case of strong electrolytic solution because they are completely ionized.

<u>Ostwald</u> discovered the relation between the degree of ionization - alpha (α) and concentration (C) mol / L for the solutions of weak electrolytes.

$$K_a = \alpha^2 \times C_a$$
 $\therefore \alpha = \sqrt{k_a/c_a}$

 $Degree of dissociation = \frac{Number of dissociated moles}{Total number of moles before dissociation}$

<u>Ostwald law of dilution :-</u> At a constant temperature, the degree of ionization () increases by dilution (K_a remains constant). where as dilution increases (concentration decreases) the degree of ionization increases and vice versa.

Calculation of hydronium ion concentration of weak acids :

$$\therefore [H_3O^+] = \sqrt{C_a x K_a}$$

Calculation of the hydroxyl ion of weak bases :

$$K_{b} = \frac{[OH^{-}]^{2}}{C_{b}}$$
, $[OH^{-}] = \sqrt{C_{b}xK_{b}}$

$$K_b = \frac{[OH^-]^2}{C_b}$$
, $[OH^-] = \sqrt{C_b x K_b}$

2 - Ionization of water:

$$K_w = [H^+][OH^-] = 10^{-14}$$
 $K_w = [10^{-7}][10^{-7}] = 10^{-14}$

K w(ionic product of water):

The result of multiplication of the concentration of hydrogen ion [H⁺] and hydroxide ion [OH] that produced from the ionization of water that equals 1X10⁻¹⁴.

Since water is neutral to litmus, the concentration of H^+ that responsible for the acidic properties equals the concentration of OH^- that responsible for the basic properties.

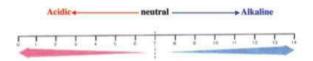
Then
$$K_w = [10^{-7}][10^{-7}] = 10^{-14}$$

pH value: It is the negative logarithm of the concentration of hydrogen ion (of base 10).

$$pH = -log [H_3O^+]$$
, $pOH = -log [OH^-]$

This is a way for expressing the degree of acidity or alkalinity for aqueous solution by numbers from zero to 14.

$$pK_w = pH + pOH = 14$$



The following table illustrates the pH values of some solutions

	Substance	PH
+	1 molar solution of HCl	Zero
	0.1 molar solution of HCl	1.0
	Gastric solution	1.6-1.8
	Lemon juice	2.3
	Acetic acid (Vinegar)	2.9
idic	Orange juice	3.5
ě.	Grape juice	4.0
	Tomato juice	4.2
	Coffee	5.0
	Rain - water	6.2
	Milk	6.3 - 6.6
1	Urine	5.5-7
Ne	eutral Pure Water	7.0
1	Saliva	6.2 - 7.4
	Blood	7.35 - 7.45
	Sea water	8.4
9	Bile juice	7.8 -8.6
Alkaline	Magnesia emulsion	10.5
Ž	0.1 Molar solution of ammonia	11.0
	Washing soda	12.0
	0.1 Molar of sodium hydroxide solution	13.0
+	1 Molar solution of sodium hydroxide	14.0

3 – Hydrolysis of salt solution :

Experiment	Observation	Conclusion
1. action of Na ₂ CO ₃ solution	turns litmus blue	alkaline solution
2. action of NH ₄ Cl solution	turns litmus red	acidic solution
3. action of CH ₃ COONH ₄	no action on litmus	neutral solution
4. action of NaCl solution	no action on litmus	neutral solution

Strong aids

Hydrochloric acid HCl \rightarrow chloride Cl⁻ Nitric acid HNO₃ \rightarrow Nitrate NO₃ -Sulphuric acid H₂SO₄ \rightarrow Sulphate SO₄²-

strong bases

potassium hydroxide KOH→K⁺ sodiumum hydroxide NaOH→Na⁺

1. Hydrolysis of sodium carbonate: (a salt of a weak acid and a strong base)

$$2H_2O$$
 $2H^+ + 2OH^-$
 Na_2CO_3 $CO_3^{2-} + 2Na^+$
 $Na_2CO_3+2H_2O$ $Na_2CO_3+2H_2O$ Na_2CO_3

2. Hydrolysis of ammonium chloride: (a salt of a strong acid and a weak base):

$$H_2O$$
 $H^+ + OH^ NH_4CI$ $CI^- + NH_4^+$
 $NH_4CI + H_2O H^+ + CI^- + NH_4OH$

3. Hydrolysis of ammonium acetate (a salt of a weak acid and a weak base):

$$H_2O$$
 \longrightarrow $H^+ + OH^ CH_3COONH_4$ \longrightarrow $CH_3COO^- + NH_4^+$
 $CH_3COONH_4 + H_2O$ \longrightarrow $CH_3COOH + NH_4OH$

4. Hydrolysis of sodium chloride: (Salt of a strong acid and a strong base):

$$NaCl \longrightarrow Cl^{-} + Na^{+}$$

$$H_{2}O \longrightarrow H^{+} + OH^{-}$$

$$NaCl + H_{2}O \longrightarrow Na^{+} + OH^{-} + H^{+} + Cl^{-}$$

From the previous we conclude that the hydrolysis process is opposite to the neutralization process. By dissolution of a salt in water, the acid and alkali from which the salt is derived are formed. The acidic or basic properly of the salt solution depends upon the respective strength of both the acid and the alkali formed due to the solution of the salt in water.

4 – Solubility product

Degree of solubility

<u>Solubility product for any sparingly soluble ionic compound is</u> the product of multiplication of the concentration (expressed as mole / liter) of its ions, raised to the power of the number of ions, which exist in equilibrium with its saturated solution.

Concentration of saturation solution for sparingly soluble salt at certain temperature(mol/L).

EX. solubility of potassium nitrate KNO₃ in water = 31.6 g / 100 ml at 20°C where solubility of silver chloride in water at same temperature = 0.0016 g / 100 ml PbBr_{2(s)} Pb²⁺_(aq) + 2Br⁻_(aq) K_{sp} = [Pb²⁺] [Br⁻]²

Chapter 4 Electrochemistry

The galvanic cell for any two elements can be represented by a diagram as shown in the following:

 Zn^{0} $/Zn^{2+}$ $//Cu^{2+}$ $//Cu^{0}$

The ELECTROMOTIVE SERIES of Elements

Half cell Half reaction	Standard oxidation potential (volt)	Standard reduction potential (volt)
Li ∢=== Li ⁺ +e	+3.045	- 3.045
K	+2.924	-2.924
Na \bullet \bullet \bullet \bullet \bullet	+2.711	-2. 71 1
$Mg \leftarrow Mg^{2+}+2e^{-}$	+2.375	- 2. 37 5
Al ∢ === ≯ Al ³⁺ +3e	+1.670	- 1. 670
Mn ∡ === ≯ Mn ²⁺ +2e ⁻	+1.029	- 1. 02 9
$Zn = Zn^{2+} + 2e^{-}$	+0.762	- 0. 762
$Cr \leftarrow Cr^{3+} + 3e^{-}$	+0.740	- 0. 740
$\operatorname{Cr} \bullet = = - \operatorname{Cr}^{2+} + 2e^{-}$	+0.557	- 0. 557
$Cr^{2+} \leftarrow Cr^{3+} + e^{-}$	+0.410	-0. 410
Fe 4 === ≯ Fe ²⁺ +2e ⁻	+0.409	- 0.409
Cd ∢=== Cd ²⁺ +2e	+0.402	-0.402
Co ∢=== Co ²⁺ +2e ⁻	+0.280	-0.280
Ni ∢=== Ni ²⁺ +2e ⁻	+0.230	-0.230
Pb ∢=== Pb ²⁺ +2e ⁻	+0.126	-0.126
$H_2 \leftarrow 2H^+ + 2e^-$	Zero	Zero
$Sn^{2+} = Sn^{4+} + 2e^{-}$	-0.150	+0.150
Cu ∢ === > Cu ²⁺ +2e ⁻	-0.340	+0.340
4OH ∢ == ≥ 2H ₂ O+O ₂ +4e	-0.401	+0.401
Ag $4 = 2 \times Ag^+ + e^-$	-0.800	+0.800
Pt ₹===≯ Pt ²⁺ +2e	-1.200	+1.200
Au ∢=== Au ³⁺ +3e	-1.420	+1.420
2F	-2.870	+2.870

Calculating electromotive force:

The electromotive force for the galvanic cell (emf)

(emf) = the reduction potentials difference for the two half cells

emf = the oxidation potentials difference for the two half cells

emf = summation of oxidation and reduction potentials of the two half cells

Galvanic cell and production of electric energy

1- Primary cells

A- Mercury cell:

Oxidation
$$Zn^{0} + HgO \rightarrow ZnO + Hg^{0}$$
Reduction
Reduction

B-Fuel cell:

At anode (oxidation reactions):

$$2H_{2(g)} + 4OH_{(aq)} \longrightarrow 4H_2O_{(v)} + 4e^-$$
 E° = 0.83V (oxidation)

At cathode (reduction reactions):

$$O_{2(g)}$$
 + 2H₂O +4e⁻ \longrightarrow 4OH⁻(aq) $E^{\circ} = 0.4$ (reduction)

The total reaction:

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(v)} E_{cell} = 1.23 V$$

2- Secondary cells

I-Lead – Acid Battery:

A - Discharging reaction: these reactions occur during battery discharge:

At the anode:

$$Pb_{(s)} + SO_4^{2-} \rightarrow PbSO_{4(s)} + 2e^{-} E=0.36V$$
(standard oxidation potential) = +0.36 volt

At the cathode:

$$PbO_{2(s)} + 4H^{+} + SO_{4}^{2-} + 2e^{-} \rightarrow PbSO_{4(s)} + 2H_{2}O E=1.69V$$

(standard reduction potential) = +1.69 volt

The cell works here as a galvanic cell and at discharging the total battery reaction is

B - Charging reaction:

Total reaction during charging

Total reaction

$$\begin{array}{c|c} P\,b + P\,b\,O & _{2} + 4\,H & _{}^{+} + 2\,S\,O & _{4}^{2} \\ \hline (s) & (s) & (aq) & (aq) & \\ \hline \end{array} \underbrace{ \begin{array}{c} disc\,harging \\ \hline charging \\ \end{array}} \begin{array}{c} 2\,P\,b\,S\,O & _{4} + 2\,H & _{2}O \\ (s) & (s) & \end{array}$$

II -Lithium ion battery:

The following reactions take place during the operation of the battery:

At anode:
$$LiC_{6(s)} \longrightarrow C_{6(S)} + Li^{+}_{(aq)} + e^{-}$$

At cathode:
$$CoO_{2(s)} + Li^+_{(aq)} + e^- \longrightarrow LiCoO_{2(s)}$$

The total reaction:
$$LiC_{6(s)} + CoO_{2(s)} \stackrel{\text{discharge}}{\longleftarrow} C_{6(s)} + LiCoO_{2(s)}$$

The emf of the battery $E_{cell} = 3V$

Iron rusting:

Iron and steel corrosion mechanism can be explained as following:

Iron acts as anode, the oxidation reaction takes place as following equation.

$$2Fe(s) \longrightarrow 2Fe^{2+}(aq) + 4e$$

The iron ion Fe²⁺ becomes a part of the electrolytic solution and the electrons transfer through the piece of iron to the cathode (carbon impureties in iron) so iron acts as anode and external circuit.

At cathode the oxygen of air is reduced in to a hydroxide group (OH)-

$$2H_2O_{(\ell)} + O_{2(g)} + 4e^- \longrightarrow 4(OH)^-_{(aq)}$$

Iron ions Fe²⁺ are combined with hydroxide ions (OH) to produce iron II hydroxide.

$$2\text{Fe2}^{+}_{(aq)} + 4\text{OH}^{-}_{(aq)} \longrightarrow \text{Fe(OH)}_{2(s)}$$

Iron II hydroxide will be oxidized by oxygen dissolved in water in to iron III hydroxide.

$$2\text{Fe}(OH)_{2(s)} + \frac{1}{2} O_{2(g)} + H_2O_{(\ell)} \longrightarrow 2\text{Fe}(OH)_{3(s)}$$

By addition of the previous equations we obtain the total equation for cell of iron corrosion.

$$2Fe_{(s)} + 3H_2O_{(0)} + 3/2 O_{2(g)} \longrightarrow 2Fe(OH)_{3(s)}$$

The rust is a slow process due to the presence of limited amounts of ions in water and it increases if a big amount of ions exists in water as in sea water.

Protection of metal against corrosion:

In the following some methods of protection of iron against rusting, by covering it by another substance to insulate it from the surrounding medium

a- Cathodic protection (Cathodic cover):

covering the metal by another less active metal

b-Anodic protection: (Anodic cover)

covering the metal by another more active metal.

Secondly: Electrolytic cells.

<u>The electrolysis:</u> It is a chemical decomposition of the substance due to the effect of passing electric current in the electrolyte.

Faraday's Laws of Electrolysis

Faraday's First Law The quantity of material (gas or solid) formed or consumed at any electrode is directly proportional to the quantity of electricity that passes in the electrolytic (solution or molten).

<u>Faraday's Second Law</u> The masses of the different materials formed or consumed by the same amount of electricity that passes in different electrolytes connected in series are proportional to their equivalent masses.

Faraday's second Law can be expressed mathematically as:

 $\frac{\text{the mass of the first element}}{\text{the mass of the second element}} = \frac{\text{the equivelent mass of the first element}}{\text{the equivelent mass of the aecond element}}$

The gram equivalent mass of the substance is the mass of the substance that has the ability to lose or gain one mole of the electrons during the chemical reaction.

the gram atomic mass

The gram equivalent mass = $\frac{C}{\text{number of charges on the ion of the element (Z)}}$

Quantity of electricity (coulomb) = current strength (ampere) x time (second)

$$[1 C = 1 A X 1 S]$$

Faraday:

On passing a quantity of electricity which if it is passed for one second in a solution of silver ions a 1.118 milligram of silver are precipitated.

The faraday unit: the quantity of electricity required to deposit or to dissolve the gram equivalent mass of any other element, according to faradays second law. where one faraday (F) =96500 C.

General Law of electrolysis:

When one faraday(1F) (96500C) passes through an electrolyte, this will lead to dissolution or evolution or deposition of gram equivalent mass of the substance at any electrode.

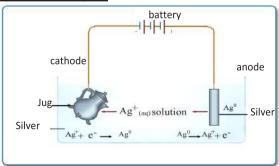
Generally the mass of deposited substance can be calculated by the following relationship mass of deposited substance (in gram)

 $= \frac{\text{current strength(amperes)x time(seconds) xequivalent mass of deposited substance}}{96500}$

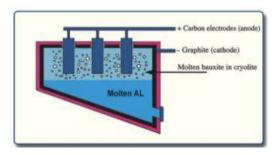
the quantity of electricity necessary to deposit gram/ atom=Faraday(F)xValence(Z)

Applications on electrolysis

1 - Electroplating



2 - Extraction of aluminum



In this cell the cathode is the body of the cell container which is made from iron plated by layer of carbon (graphite) ,while the anode is carbon rods (graphite). When the electric current passes between the cell electrodes an oxidation – reduction reaction occurs:

At the cathode (-):

$$2Al^{3+}+6e^{-} \xrightarrow{\text{reduction}} 2Al$$

At the anode (+):

$$3O^{-2} \xrightarrow{oxidation} \frac{3}{2}O_{2} + 6e^{-1}$$

And the total reaction is:

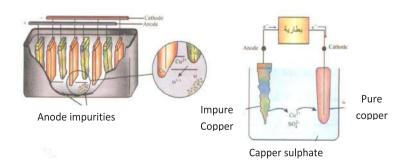
$$2 \text{ Al}^{3+} + 3 \text{O}^{2-} \longrightarrow 2 \text{Al} + \frac{3}{} \text{O}_2 \text{ (g)}$$

The evolved oxygen reacts with the carbon electrodes forming carbon mono and dioxides

$$3/2O_{2(g)} + 2C_{(s)} \longrightarrow CO_{(g)} + CO_{2(g)}$$

Then aluminum is withdrawn from the cell through a special opening.

3 – Purification of Metals



At anode:
$$Cu_{(s)}$$
 \longrightarrow $Cu^{2+}_{(aq)} + 2e^{-}$

At cathode:
$$Cu^{2+} + 2e^{-} \longrightarrow Cu_{(s)}$$

While the impurities:

$$Zn^0_{(s)}$$
 \longrightarrow $Zn^{2+}_{(aq)}$ $+2e^-$
 $Fe^0_{(s)}$ \longrightarrow $Fe^{2+}_{(aq)}$ $+2e^-$

These ions still in the solution, While silver and gold impurities fall down the anode.

Chapter 5 Organic chemistry

Vital Force theory

Berzelius considered that organic compounds are formed by vital force which is found in living cells of the body and it is impossible to synthesize them in laboratories.

In 1828, The German scientist **Wöhler** destroyed the vital force theory, when he prepared urea (organic compound formed in the urine of mammals) by heating an aqueous solution of two inorganic compounds, ammonium chloride and silver cyanate.

$$\begin{array}{l} NH_{4}C1 + AgCNO_{(aq)} \xrightarrow{} AgC1 + NH_{4}CNO_{(aq)} \\ NH_{4}CNO_{(Ammonium\ cyanate)} \xrightarrow{\Delta} H_{2}N\text{-CO-NH}_{2(Urea)(s)} \end{array}$$

What are the reasons of the abundance of organic compounds?

The abundance of organic compounds is due to the ability of carbon atom to combine with itself or with others atoms by different kinds of bonds, it might connect through single, double, triple bonds.

Carbon atoms can join together with different methods, straight chains, branched chains, homocyclic or heterocyclic.

The difference between organic and inorganic compounds

Property	Organic compounds	Inorganic compounds
1-Chemical structure	- mainly contain carbon atoms.	may contain carbon atoms in addition to other elements.
2-Solubility	- most are insoluble in water but soluble in organic solvent e.g. benzene.	most are soluble in water
3-Melting point	- Low.	High
4-Boiling point	- Low.	High
5-The odour	-most have characteristic odour.	most are odourless

1		
6-Inflammability	- inflammable and produce CO ₂ , H ₂ O	not inflammable, if it is
		inflammable, it produces other gases
7-Kinds of bonds in the	- covalent bonds	ionic bonds
molecule		
8-Electrical	 don't conduct electricity. 	Usually electrolytic compounds
conductivity		conduct electricity.
9-Rate of chemical	- slow, because it takes	Often fast, because it takes place
reaction	place between the	between the ions.
	molecules	
10-Polymerization	- can be polymerized	can't be polymerized
11.7	24. 6 1	
11-Isomerism	- it's found among	It is not found among their
	many compounds	compounds.

Molecular Formula:

It is the formula which indicates the number and kind of the elements atoms which form the chemical compound, and doesn't show the kind of the linkage between the atoms in the molecule.

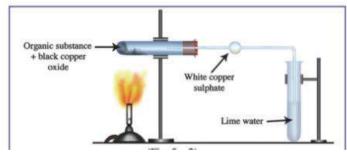
Structural Formula:

It's the formula which indicates the number and kind of each elements atoms in the molecule, and the kind of linkage between the atoms by the covalent bonds.

Isomerism:

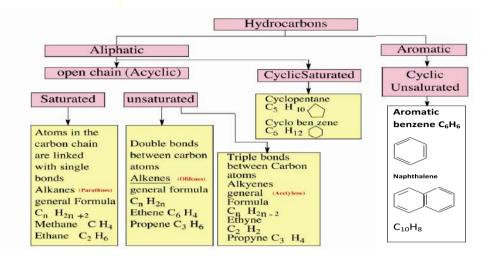
It is a phenomenon that many organic compounds are different in the physical and chemical properties and also in structural formula but they have the same molecular formula.

Detection of carbon and hydrogen in organic compound



Hydrocarbons

They are organic compounds consist of carbon and hydrogen only.



Homologous series:

It is a group of compounds that having the same general molecular formula, chemical properties and graduated physical properties like (boiling point).

The Alkyl Radical (R –):

It is an organic atomic group which does not found alone. It is derived from the corresponding alkane by removing one hydrogen atom . Alkyl radicals are given the symbol "R". Their general formula is (C_nH_{2n+1}) . Its name is derived from the corresponding alkane by replacing the suffix (ane) by (yl).

Examples		R-H Alkane C _n H _{2n+2} -H → R- Alkyl radical C _n H _{2n+1}	
Methane (CH₄	Methyl -CH ₃	Methyl chloride CH₃C ∕

The nomenclature of alkanes (IUPAC system)

The nomenclature of alkanes by the IUPAC system may be summarized as follows:

- 1- The name of the hydrocarbon is determined according to the longest continuous carbon chain which may be linear or branched.
- 2- The carbon atoms are given numbers in the longest chain.
- a- If the longest hydrocarbon chain free from any branches or side chain the carbon atoms are given numbers from any side (left or right side).b- If the longest hydrocarbon chain attached to an alkyl group or any other atoms. The numbering of carbon atoms in the hydrocarbon chain begins from the side nomenclature begins by the number of

$$C^{1}H_{3}-C^{2}H-C^{3}H_{2}-C^{4}H_{2}-C^{5}H_{3}$$
 CH_{3}

2-methyl pentane

the carbon atom from which the chain arises, then the name of the branch, and ending by the name of the alkane.

$$CH_3$$
- C^3 H- C^4 H₂- C^5 H₂- C^6 H₃

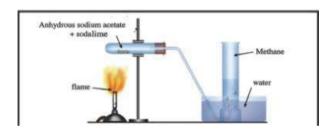
$$C^2$$
 H₂

$$C^1$$
H₃

3-methyl hexane

- 3- If the side group is repeated in the hydrocarbon chain we use prefix Di or Tri or Tetra to indicate the number of repetition.
- 4- If the branch is a group such as. Cl, Br or NO_2 , the name of this group is ended by the letter (O) so we say chloro, bromo or nitro.
- 5- If the side groups are different (alkyl group and halogens), the groups are arranged according to their alphabetical Latin names, after numbering from the end that giving the branches the least possible summation.

Preparation of methane in lab. :-



$$CH_3COONa_{(s)} + NaOH_{(s)}$$
 $CaO/4$ $CH_{4(g)} + Na_2CO_{3(s)}$

<u>a – The chemical properties: 1-Burning:</u>

$$CH_{4(g)} + 2O_{2(g)}$$
 Δ $CO_{2(g)} + 2H_2O_{(v)} + Energy$

2-The reactions with Halogens: UV or 400°C

1-
$$CH_{4(g)} + CI_{2((g)}$$
 (uv) $CH_3CI_{(g)} + HCI_{(g)}$

Chloro methane (Methyl chloride)

$$2\text{- }\text{CH}_{3}\text{Cl}_{\,(g)} + \text{Cl}_{2((g)} \quad \underline{\quad \text{(uv)} \quad \text{CH}_{2}\text{Cl}_{2(g)} + \text{HCl}_{\,(g)} }$$

Ddichloro methane (Methylene chloride)

$$\text{3- } \mathsf{CH_2Cl_{2(g)}} + \mathsf{Cl_{2((g)}} \quad \underline{\quad \text{(uv)} \quad \mathsf{CHCl_{3(g)}}} + \mathsf{HCl_{(g)}}$$

Trichloro methane (chloroform)

4-
$$CHCl_{3(g)} + Cl_{2((g)}$$
 (uv) $CCl_{4(g)} + HCl_{(g)}$

Tetrachloro methane (Carbon tetra chloride)

Uses of halogenated derivation of alkanes

- 1- Chloroform was used for a long time as anesthetic substance
- . Halothane is used now as an esthetic substance with safety and its formula CHBrCl - CF $_{\!3}$ it is 2-bromo -2-chloro -1,1,1-tri fluoro ethane.
- 2. The compound 1,1,1 trichloro ethane is used in the dry cleaning.
- 3. Freons were used in air conditions and fridges, also as a rushed substance to liquid and perfumes and as a cleaner of electronic sets.

Freons are consider as a kind of halogenated derivative of alkanes as CF_4 tetra flouro methane but the famous one is dichloro, diflouromethane CF_2 Cl_2 .

3. Thermal catalytic cracking:.

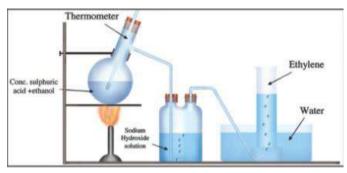
$$C_8H_{18(\cdot)}$$
 high pressure ,temp,cat $C_4H_{8(g)} + C_4H_{10(g)}$
Octane butene butane

B - Unsaturated open chain aliphatic hydrocarbons

Alkenes (Olifenes C_nH_{2n})

Preparation of Ethene in lab:

$$C_2H_5OH_{(I)}$$
 conc. (H_2SO_4) at $180^{\circ}C$ $C_2H_{4(g)} + H_2O_{(v)}$



This reaction takes place in two steps.

1- Ethanol reacts with conc. heated sulphuric acid, to form ethyl hydrogen sulphate.

Ethyl hyrogen sulphate

2- Ethyl hydrogen sulphate thermally decomposed to give ethene .

Chemical properties: 1-Burning:

$$C_2H_{4(g)} + 3O_{2(g)} \xrightarrow{\Delta} 2CO_{2(g)} + 2H_2O_{(v)} + energy$$

2- Addition reaction:

a. Addition of hydrogen(H2) (Hydrogenation):

$$CH_2=CH_{2(g)}$$
 + $H_{2(g)}$ Pt or Ni at 150to300°C $CH_3-CH_{3(g)}$ ethane

b. Addition of halogens (X2) (Halogenation):

$$CH_{2} = CH_{2} + Br_{2} \xrightarrow{CCl_{4}} H - C - C - H$$

$$(g) \qquad (g) \qquad Br \qquad Br \qquad (1,2 \text{ dibromoethane}) \qquad (I)$$

C. The addition of hydrogen halide (HX)

Markownikoff's rule:

"On adding an asymmetric reagent (HX or $H-OSO_3H$) to an asymmetric alkene, the positive part of the reagent is added to the carbon atom which carries a large number of hydrogen atoms and the negative part is added to the carbon atom which carries less number of hydrogen atoms ".

d. Addition of water (H₂O) (Catalytic hydration):

1- Addition of acid to ethene

$$CH_2 = CH_2 + HOSO_3H \xrightarrow{\Delta \\ 80^{\circ}C} CH_3 - CH_2 - OSO_3H$$

ethyl hydrogen sulphate

2- hydrolysis of ethyl hydrogen sulphate

$$\begin{array}{c} \text{CH}_3\text{-}\text{CH}_2\text{-}\text{OSO}_3\text{H} + \text{H}_2\text{O} \xrightarrow{\quad \Delta \\ \quad 110^{\circ}\text{C}} \\ \text{CH}_3\text{-}\text{CH}_2\text{-}\text{OH} + \text{H}_2\text{SO}_4 \\ \text{By addition} \\ \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\quad \text{H}_2\text{SO}_4 \\ \quad \Delta \\ \text{(g)} \end{array} \\ \begin{array}{c} \text{(A)} \\ \text{(b)} \\ \text{(b)} \end{array} \\ \text{(b)} \end{array} \\ \begin{array}{c} \text{(b)} \\ \text{(c)} \\ \text{(c)} \\ \text{(c)} \end{array}$$

3- Oxidation: Baeyr's reaction: It is the reaction between ethene and potassium permanganate in alkaline medium where the purple colour of potassium permanganate is discharged. This reaction is very important to detect the double bond.

$$\begin{array}{c} H & H \\ H - C = C - H + H_{2}O + [O] \xrightarrow{\frac{KMnO_{4}}{\text{alkaline medium}}} H - C - C - C - H \\ OH OH (ethylene glycol) \end{array}$$

4- Polymerization:

There are two principal methods for polymerization process.

1- <u>Addition polymerization</u>: The table illustrates some alkene monomers and their derivatives which are produced by addition polymerization and their uses:

Monomer	Polymer	Commercial name	Property	Uses
Ethene $ \begin{array}{ccc} H & H \\ \hline C = C \\ \hline \end{array} $	H H -C - C- H H (polyethylene)	Poly Ethylene	Soft and resist effect of chemicals	Plastic sheets, bags, bottles& hoses.
Н Н	((PE)		
н н	H H	Poly propylene	Strong and hard	Carpets, cases and
$ \begin{array}{ccc} H & H \\ C = C \\ CH_3H \end{array} $	CH ₃ H Polypropylene	p. 5p / . 6 . 10		cans.
propene	(pp)	(PP)		

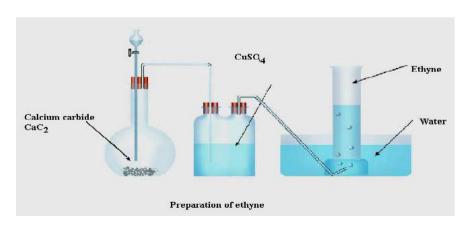
$\begin{array}{ccc} H & H \\ C = C \\ H & Cl \\ \end{array}$ Chloro ethene (vinyl chloride)	H H [-C-C- H Cl Poly chloroethane	Poly vinyl chloride (PVC)	Strong and soft	Drainage tubes- plastic, tubes- shoes - hoses — electric wires, insulators — floors- oils bottles .
F F C = C F F tetra flouro ethene	F F F Poly tetra flouro ethene	Teflon	Resist heat and adhesion, electrical insulator and inert	Cooking utensils – surgical threads.

2- <u>Condensation polymerization</u>: Condensation takes place between two different monomers and accompanied by losing a simple molecule such as water .



Ethyne (acetylene) $H - C \equiv C - H$

Preparation in lab:



$$C = C + 2 HOH_{(I)} \longrightarrow H - C = C - H + Ca(OH)_{(aq)}$$

2-Ethyne can be prepared in industry

$$2CH_{4(g)} \quad \xrightarrow[Rapid \ quenching]{1500^{\circ}} \quad C_2H_{2(g)} \quad + \ 3H_{2(g)}$$

Properties of ethyne:

1-Combustion:

$$2C_2H_2 + 3O_2 \xrightarrow{\text{heat}} 2CO_2 + 2H_2O + 2C_{\text{(s)}}$$

$$2C_2H_2 + 5O_2 \xrightarrow{\text{heat}} 4CO_2 + 2H_2O + \text{heat}$$

2- Addition reactions:

a- Hydrogenation in the presence of finely divided nickel

H-C = C-H + H₂
$$\xrightarrow{\text{Ni/ heat}}$$
 $\xrightarrow{\text{C=C}}$ $\xrightarrow{\text{C}}$ Ethyne

b- Halogenations:

$$C_2H_2 + Br_2$$
 (g)
 $C_2H_2Br_2$
 (g)

3-The addition of halogen acids (HX)

4-Addition of water (catalytic hydration)

Ethyne reacts with water by addition in the presence of a catalyst e.g H_2SO_4 , $HgSO_4$ at $60^{\circ}C$ to give acetaldehyde (ethanal).

$$\begin{array}{c} \text{H-C} \equiv \text{C-H} + \text{H}_2\text{O} \xrightarrow[\text{HgSO}_4/(60^{\circ}\text{C})]{\text{HgSO}_4/(60^{\circ}\text{C})}} \\ \text{Ethyne (g)} & (\nearrow) \end{array} \xrightarrow[\text{HgSO}_4/(60^{\circ}\text{C})]{\text{HgSO}_4/(60^{\circ}\text{C})}} \\ \begin{array}{c} \text{H OH} \\ \text{I - C = CH} \\ \text{Vinyl alcohol} \end{array} \longrightarrow CH_3CHO \\ \text{Ethanal (}\nearrow) \end{array}$$

(Unstable compound)

(Acetaldehyde)

This reaction is used to prepare ethanoic acid (acetic acid) by the oxidation of acetaldehyde (ethanal).

$$CH_3CHO_{()}$$
 $\xrightarrow{\text{Oxidation}} CH_3COOH_{()}$

Ethanol can be obtained from reduction of acetaldehyde (ethanol)

$$CH_3CHO_{(i)} \xrightarrow{H_2} CH_3CH_2OH_{(l)}$$

Secondly Cyclic hydrocarbons

a- Saturated cyclic hydrocarbons (Cycloalkanes)

 C_3H_6

 C_4H_8

C₅H₁₀

C₆H₁₂

Cyclopropane

Cyclobutane

Cyclopentane

Cyclohexane

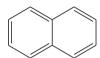
Unsaturated cyclic chain hydrocarbons(Aromatic hydrocarbons)

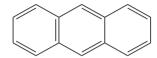
1-Aromatic benzene

2-Naphthalene

3-anthracene







Preparation of benzene in industry

- 1- From coal Tar
- 2- From aliphatic petroleum derivatives :
- a) From normal hexane:

Catalytic reforming method

$$CH_3-CH_2-CH_2-CH_2-CH_3$$
 \triangle \triangle \triangle \triangle \triangle \triangle benzene

b) Polymerization of ethyne:

$$3C_2H_2 \xrightarrow{\text{red hot}} \bigcirc$$

3- From phenol:



Preparation of benzene in lab.

$$(s)$$
 (s) (a) $CaO + heat$ (b) $+Na_2CO_3$ (b) (c) (d) (d)

Nomenclature of disubstituted benzene derivatives:

2-The disubstituted benzene may be represented by three isomers which are: ortho (o-) meta (m-) and para (p-).

The product depends on the nature of the substituent group which is mainly found.

There are some groups direct the new substituent to **ortho** and **para** positions and other direct to **meta** position.

From groups which is directed to ortho and para positions are the alkyl group(-R) , hydroxyl group(-OH), amino groups $(-NH_2)$ and halogen atoms(X-)

From the meta directing groups are the aldehydic group(-CHO), ketonic group (-CO), carboxylic group(-COOH) and Nitro group(-NO₂).

Chemical properties

a) Addition reactions:

1- The addition of hydrogen (hydrogenation):

2- Halogenation:

$$C_6H_6Cl_6$$
 CI
 CI

b) Substitution reaction:

1- Halogenation

3- Alkylation (Friedel - craft's reaction):

2- Nitration

Toluene
$$(7)$$
 (7) (7) (7) (7) (7) (7) (7) (7) (8) (8) (8) (8) (8) (9) (9) (9) (9) (1) $(1$

4- Sulphonation :

The detergent industries depend mainly on the aromatic sulphonic acid compounds after the treatment with caustic soda to obtain the water-soluble sodium salt.

R—SO₃H +NaOH
$$\longrightarrow$$
 R—SO₃H + H₂O

Alkyl benzene sulphonic acid

Sodium salt of alkyl benzene sulponic acid

(detergent)

The molecule of detergent is composed of two parts (tail), it is a long carbon chain which is hydrophobic and the other part (head), is an ionic group which is hydrophilic.

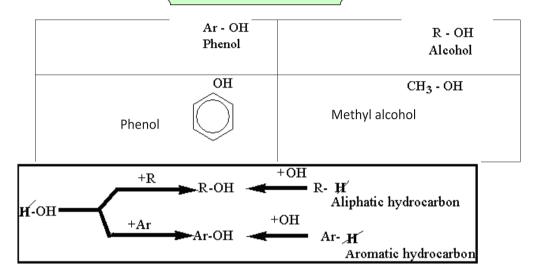
Hydrocarbon derivatives

The following table illustrates the classes of the organic compounds and their functional group:

The class	General formula	The functional group	example
Alcohols	R – OH	The hydroxyl — OH	Methyl alcohol CH₃OH
Phenols	Ar – OH	The hydroxyl –OH	Phenol
Ethers	R – O – R	Etherial – O –	Dimethyl ether $CH_3 - O - CH_3$
Aldehydes	R – CHO	Formyl $\overset{\text{H}}{-C} = O$	Acetaldehyde CH_3-CHO
Ketones	O R - C- R	Carbonyl – C = O	Acetone $ \begin{matrix} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ \end{matrix} $
Carboxylic acids	O R - C- OH	Carboxylic – COOH	Acetic acid CH₃COOH

Esters	O R - C- OR	Ester – COOR	Ethyl acetate ester CH₃COOC₂H₅
Amines	R – NH ₂	Amino - NH ₂	Ethyl amine C ₂ H ₅ NH ₂

Alcohols and phenols



1-Alcohols

Nomenclature of alcohols: There are two methods

a- According to the alkyl group (Common nomenclature):

In this methods the alcohol is named according to the name of alkyl group present in the alcohol molecule. The word alcohol is added to the name of the alkyl group e.g methyl alcohol C_3OH , ethyl alcohol C_2H_5OH .

b- The nomenclature according to IUPAC:

The name of alcohol is derived from the name of the corresponding alkane (which contains the same number of carbon atoms) then adding the suffix "ol" instead of "e" like CH_3OH methanol, C_2H_5OH ethanol. In this system the carbon chain is numbered from the nearest end to the hydroxyl group.

N.B. In case of common nomenclature, the name "iso" is used if the terminal carbon atom in a continuous chain is attached to two methyl groups and hydrogen atom.

$$CH_3 - CH_2 - CH_2 - OH$$
 $CH_3 - CH - OH$ I CH_3

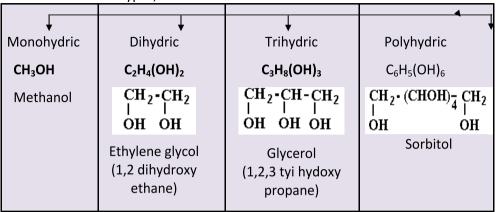
Normal propyl alcohol iso propyl alcohol

or 1- propanol

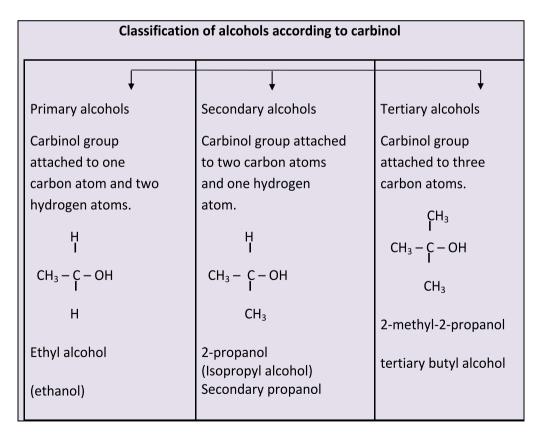
or 2 - propanol

Classification of alcohols.

Alcohols are classified according to the number of hydroxyl groups in the alcohol molecule into four types, these are:



Monohydric alcohols are classified into three kinds according to the type of carbinol group (carbon atom attached to the hydroxyl group).



Monohydric Primary Alcohols

Ex: Ethyl alcohol (ethanol) C₂H₅OH

Methods of preparation of ethanol (in industry)

1- By alcoholic fermentation:

$$\begin{array}{ccc} C_{12}H_{22}O_{11} + H_2O & \xrightarrow{hydrolysis} & C_6H_{12}O_6 + C_6H_{12}O_6 \\ \text{Sucrose} & (\nearrow) & \text{glucose fructose} \end{array}$$

$$\begin{array}{c} C_{6}H_{12}O_{6} \xrightarrow{\text{yeast} \\ \text{(aq)}} 2C_{2}H_{5}OH + 2CO_{2} \\ \text{(g)} \\ \text{ethanol} \end{array}$$

2- By catalytic hydration of ethene

Petroleum product
$$\xrightarrow{\text{cracking}}$$
 $CH_2 = CH_2 + H_2O \xrightarrow{\text{H}_2SO_4}$ C_2H_5OH (g) ///

N.B. Ethene is the only alkene which gives primary alcohol by catalytic hydration, while the other alkenes give secondary or tertiary alcohols (Markownikoff's rule)

$$CH_3-CH=CH_2 \xrightarrow{+H_2O \xrightarrow{H_2SO_4}} CH_3-CH-CH_3$$

$$(1) \xrightarrow{(1)} OH$$

$$2 \text{ prepare} (See else bel)$$

propene

2-propanol(Sec.alcohol)

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3}\text{-}\overset{\mid}{\text{C}} = \text{CH-CH}_{3} + \text{H}_{2} \\ \text{OH} \end{array} \xrightarrow{\begin{array}{c} \text{H}_{2}\text{SO}_{4} \\ \text{110}^{0}\text{C} \end{array}} \begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3}\text{-}\overset{\mid}{\text{C}} \text{-CH}_{2}\text{-CH}_{3} \\ \text{OH} \end{array}$$

2 -butene

2-Methyl-2-butanol[Tert.alcohol]

The converted alcohol: (red spirit)

Pure ethanol of 96% concentration is expensive because of the high production tax which should be paid for it. This is imposed to minimize its use in making alcoholic liquors because of their harmful effect on health and social aspects. However, ethanol is very important as fuel, in the chemical industries and organic solvent. Some additives are added to ethanol to be used as fuel with low price. These poisonous additives like methanol (causes madness and blindness), pyridine (with bad odour)

and coloured dyes. These additives cannot be easily separated from alcohol except with very complicated chemical processes besides, it is illegal.

The general method of Preparation of alcohols:

$$RX + KOH_{(aq)} \xrightarrow{\Delta} R - OH + KX$$

N.B. Halides may be arranged in the following sequence according to the ease of displacement. Chlorides < bromides < iodides

where R =the alkyl radical , X =halide radical.

General properties of alcohols

The physical properties:

Alcohols especially the first members are completely soluble in water and their boiling points are relatively high.

The solubility in water and the high boiling points of alcohols are attributed to the presence of the polar hydroxyl groups

Alcohol	Boiling point
C ₂ H ₅ OH	78°C
ethanol	
C ₂ H ₄ (OH) ₂	197°C
ethylene glycol	
C ₃ H ₄ (OH) ₃	290°C
glycerol	

which have the ability of forming hydrogen bonds either between the alcohol molecules themselves or between the alcohol molecules and the water molecules

Chemical properties:

The chemical properties of alcohols may be classified as follows:

- 1- Reactions specific to hydrogen of the hydroxyl group.
- 2- Reactions specific to the hydroxyl group.
- 3- Reactions specific to the carbinol group.
- 4- Reactions specific to the whole molecule.

1- Reaction specific to the hydrogen of the hydroxyl group. a- Acidity of alcohols.

We have mentioned that alcohols have neutral effect on litmus, but a weak acidic character may appear specially when it reacts with strong active metals e.g sodium or potassium which can replace the hydrogen of the hydroxyl group.

2 R - OH+2 K
$$\rightarrow$$
 2 ROK $_{\text{potassium alkoxide}}$ + H_2

$$2C_2H_5OH +2Na \longrightarrow 2C_2H_5ONa +2H_2 \uparrow_{burns \ with \ pop \ sound}$$

$$(\cancel{g}) \qquad (g)$$

b- Ester formation:

$$\text{CH}_{3}\text{CO}^{16}\text{O}^{16}\text{H} + \text{C}_{2}\text{H}_{5}\text{O}^{18}\text{H} \xrightarrow{\text{H}_{2}\text{SO}_{4}} \text{CH}_{3}\text{COOC}_{2}\text{H}_{5(aq)} + \text{H}_{2}\text{O}^{16}$$

2- Reactions specific to the hydroxyl group.

$$C_{2}H_{5}OH + HCl \xrightarrow{ZnCl_{2}} C_{2}H_{5}Cl + H_{2}O$$

$$() () () ()$$

3-Reactions specific to carbinol group:

a- Oxidation of primary alcohols:

b- Oxidation of secondary alcohols:

c- Oxidation of tertiary alcohols:

Since carbinol group is not attached with any hydrogen atoms, it is difficult to be oxidized under these conditions.

4- Reaction specific to the whole molecule:

$$\begin{array}{c} H \\ H \\ H - C - C - OH \\ H \end{array} \xrightarrow{H_2SO_4 - (180^0c)} H_2C = CH_2 + H_2O \\ (9) \end{array} \quad (v)$$

$$\begin{array}{c} \text{C_2H}_5$OH \\ & \xrightarrow{\text{H_2SO}_4$ conc.} \\ \text{C_2H}_5$OH \\ & \swarrow \end{array} \\ \begin{array}{c} \text{H_2SO}_4 \text{ conc.} \\ \text{140°C} \end{array} \\ \begin{array}{c} \text{C_2H}_5$-O-C_2$H}_5 + \text{H_2O} \\ \text{$diethylether} \end{array} \\ \text{(g)} \end{array}$$

The economical important of alcohol (uses of alcohol):

- 1- They are used as solvents for organic compounds as oils and fats and used in chemical industries e.g. preparation of drugs, paints and polishes.
- 2- Ethanol is used in sterilizing mouth and teeth also it is used as disinfectant which has a great effect on killing microbes.
- 3- Ethanol is used in the manufacture of perfumes and alcoholic liquors. We must put into consideration the bad effect of alcoholic drinks for man's heath, like the liver fibrosis, cancer of stomach and oesophagus.
- 4- It may be mixed with gasoline which is used as a fuel. In some countries, such as Brazil.
- 5- It is the main component of converted alcohol (85% ethanol + 5% methanol + 1% another additive + colour, odour and the rest is water).
- 6- Ethanol freezes at (-110°C) so it is used to fill special thermometers which measure the lower temperature until (50°C) as it has low freezing point (-110.5°c).

2- Dihydric alcohols:

e.g:

H₂C — CH₂

| Ethylene glycol
OH OH (1,2 dihydroxy ehane)

- 1- It is used as antifreeze substance in car radiators in cold countries.
- 2- Due to its high viscosity it is used as a constituent of the liquids used in the hydraulic break in addition it is used in printing ink.
- 3- It is used to prepare polyethylene glycol (PEG) which is used in the manufacture of Dacron fibers, photographic films and cassette tapes.

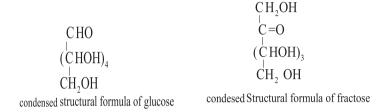
3- Trihydric alcohols . CH2—CH—CH2
Glycerol (1,2,3 trihydroxy propane) OH OH OH

- 1- It is used in the manufacture of creams and cosmetics as a moisturizer of skin.
- 2- It is used in the manufacture of textiles, since it renders them soft and flexible.

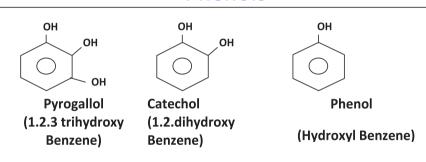
3- It is used in the preparation of explosive substance nitroglycerine obtained by nitration of glycerin by a mixture of concentrated, nitric and sulphuric acids.

Nitroglycerine is also used to widen arteries in the treatment of heart problem.

4- Polyhydric alcohols



Phenols



-Phenol (carbolic acid) C₆H₅OH:

Preparation of phenol.

- 1- From fractional distillation of coal tar.
- 2- From halogenated aromatic compounds, by the hydrolysis of chlorobenzene with sodium hydroxide at high temperature and high pressure 300 atmospheres.

Physical properties:

Phenol is a solid corrosive substance. It has a characteristic odour, melts at 43°C. Phenol is sparingly soluble in water, its solubility in water increases by raising the temperature, it becomes completely miscible with water at 65°C.

Chemical properties:

1- Acidity of phenol compared to alcohols:

Points of comparison	R-OH alcohol	OH
Reaction with sodium metal	R-ONa+H₂	ONa + H ₂
Reaction with sodium hydroxide	No reaction	ONa + H ₂ O

2- Rection of phenol with halogen acids compared to alcohols:

Point of comparison		OH J
	R-OH	
	Alcohol	phenol
Reaction with HCl	RCI +H ₂ O	Do not react due to the strong bond between oxygen and benzene ring.

3- Nitration of phenol:

OH
$$OH$$
 OH OH OOH OOD OOD

Trinitrophenol(Picric acid)

$$\begin{array}{c} H \\ | \\ \end{array}$$
 4- With formaldehyde : H-C=O

Phenol reacts with formaldehyde in acidic or alkaline medium to form copolymer, then polymerization process takes place by condensation to form bakelite polymer.

Detection of phenol.

- 1- On adding few drops of iron III chloride solution to phenol, a violet colour is produced.
- 2- On adding bromine water to phenol, a white precipitate is produced.

Carboxylic acids

Carboxylic acids are characterized by the presence of one or more carboxylic group (-COOH). The carboxylic group may be attached to an alkyl radical to give an aliphatic acid, or attached directly to a benzene ring and give aromatic acids.

OH
$$\begin{array}{c}
OH \\
R-C=O
\end{array}$$
Aromatic acid

OH
$$R-C=O$$
Aliphatic acid

The saturated monocarboxylic aliphatic acids are named fatty acids because many of them are present in fats in the form of ester with glycerol.

The carboxylic group (-COOH) is the functional group of organic acids . It is composed of two groups i.e. the carbonyl group and the hydroxyl group \searrow_{C-O} (-OH).

Types of carboxylic acids:

A) Monocarboxylic acids (Monobasic)



B) Diccarboxylic acids (Dibasic acids)



Nomenclature of carboxylic acids

<u>The common names:</u> The carboxylic acids are usually named by common names which are derived from the Latin name of the source from which the acid is prepared. **IUPAC nomenclature:**

The common name of acids are more used than the other common names of organic compounds. In the (IUPAC) nomenclature of acids, the name of the acid is derived from the name of the corresponding Alkane that contains the same number of carbon atoms by adding the suffix (oic) to the name of alkane instead of the letter (e).

The following table shows the common and (IUPAC) names of some carboxylic acids.

Formula	Common name	Corresponding alkane	IUPAC
НСООН	Formic acid Ants Ant (Formica)	Methane	Methanoic acid
CH₃ COOH	Acetic acid Vinegar (Acetum)	Ethane	Ethanoic acid
C ₃ H ₇ COOH	Butyric acid Butter (Butyrum)	Butane	Butanoic acid
C ₁₅ H ₃₁ -COOH	Palmetic acid (Palm oil)	Hexadecane (Contain16 carbon atoms)	Hexadecanoic acid

Acetic acid:

The methods of preparation of acetic acid in industry:

1- Biological method:

Acetic acid (Vinegar) is prepared in (Egypt) by the oxidation of diluted alcoholic solutions by atmospheric oxygen in the presence of a special type of bacteria known as vinegar bacteria.

2- Preparation from acetylene:

Acetic acid is prepared in industry on a large scale by catalytic hydration of acetylene where acetaldehyde is produced, which is easily oxidized to the acid.

$$H-C \equiv C-H + H_2O \xrightarrow{H_2SO_4 (40\%)} H_3 - C = O \xrightarrow{H_2SO_4 (40\%)} CH_3 - C = O \xrightarrow{(A)} C$$

General properties of aliphatic acids:

Physical properties:

By comparing the boiling points of carboxylic acids with those of alcohols which have the same number of carbon atoms, we find that the boiling point of acids are higher. This is attributed to the association of molecules by hydrogen bonds. Each acid molecule is linked to another molecule by two hydrogen bonds.

Acid	Molecular mass	b.p °C	Alcohol	Molecular mass	b.p° C
Formic	46	100	Ethanol	46	78
Acetic	60	118	Propanol	60	98

Chemical properties

- 1- Reactions attributed to the hydrogen ion:
- * Acidity and salt formation:

$$2 \ CH_{3}COOH_{(aq)} + Mg_{(s)} \longrightarrow (CH_{3}COO)_{2}Mg_{(aq)} + H_{2 (g)}$$

$$Magnesium \ acetate$$

$$CH_{3}COOH_{(aq)} + NaHCO_{3(s)} \longrightarrow CH_{3}COONa_{(aq)} + H_{2}O_{(i)} + CO_{2(g)}$$

$$sodium \ acetate$$

- 2- Reactions attributed to hydroxyl group
- * Ester formation

Organic acids reacts with alcohols to form ester and water.

O
$$R-C = OH + H-OR \xrightarrow{H_2SO_4} R-C = O+H_2O$$

3- Reactions attributed to the carboxylic group:

Carboxylic acids are reduced by hydrogen in the presence of copper chromate $CuCrO_4$ at 200°C as a catalyst. Ethanol may be prepared from acetic acid by this method. This reaction is opposite to that of oxidation of alcohols to acids.

O
$$CH_3 - C - OH + 2H_2 \xrightarrow{CuCrO_4} CH_3 - CH_2 - OH + H_2O$$
 (aq)
 (g)
 (g)

Detection of acetic acid:

1- Acidity test.

2- Ester formation test.

Aromatic Carboxylic acids

Benzoic acid can be prepared commercially by the oxidation of toluene by the proper oxidizing agent. It is prepared commercially by the oxidation of toulene in atmospheric air at 400° C and in the presence of vanadium pentoxideV₂O₅.

2
$$V_2O_5$$
 $O(g)$
 $O(g$

Aromatic acids are generally stronger, less soluble in water and less volatile than aliphatic acids. The reaction of the carboxylic group resembles that of aliphatic acids. This can be represented by the formation of salts with metals, their hydroxides or carbonates and the formation of esters with alcohols.

COOH

COONa

+ NaOH

(aq)

Sodium benzoate

COONa

$$(aq)$$

Figure 1

 (aq)

Sodium benzoate

$$\begin{array}{c|c} COOH & COOC_2H_5 \\ \hline & + C_2H_5OH & dry \ HCl & (aq) \\ \hline & Benzoic \ acid & Ethyl \ benzoate \\ \end{array}$$

Carboxylic acids in our life:

1- Formic acid:-

It is used in the manufacture of dyes , insecticides, perfumes, drugs and plastics.

2- Acetic acid:

It is considered as a starting material for the synthesis of many organic products.

e.g. synthetic silk, dyes , insecticides and food additives.

3-Benzoic acid:

Sodium benzoate 0.1% is used as foods preserving substance, because it prevents the growth of fungi on foods.

4- Citric acid:

It prevents the growth of bacteria

in foods because it decreases their (pH) .It has many

H H-C-COOH HO-C-COOH H-C-COOH

industrial uses, and is added to frozen fruits to retain their

colour and taste OH

5- Lactic acid CH₃ - CH-COOH

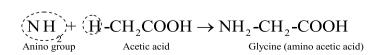
6- Ascorbic acid vitamin (c):

Lack of vitamin C leads to deterioration of some biological functions in the human body and the infection whith "Escarpot" disease, from its symptoms, bleeding of gum and joints swelling.

7- Salicylic acid

It is used in the manufacture of cosmetics specific to skin, because it make it more soft, flexible and protect it against sun rays and in elimination of skin warts and acne. It is also used in preparation of Aspirin.

8- Amino acids



The amino acids which form proteins are of the (α) amino type , i.e. the amino group is attached to the (α) carbon atom which is directly attached to the carboxylic group.

Proteins are considered as polymers of amino acids

Esters

Esters are the products of the combination of carboxylic acids with alcohols. This can be represented by the general formula.

$$R-C-OR + H_2O$$
Acid Alcohol Ester

The name of an ester is derived from the name of the acid radical and the name of the alkyl group of the alcohol as shown by the following examples

HCOOCH₃ CH₃COOCH₂CH₃ COOC₂H

Methyl formate Ethyl acetate Ethyl benzoate

The direct method for the preparation of esters, is the reaction between the carboxylic acid and the alcohol. For example, the ethyl acetate is obtained by the reaction of acetic acid and the ethyl alcohol.

Physical properties:

The		The acid	Alcohol	Ester
molecular weight =		Acetic acid	propanol	Methyl
60 g/mol		CH₃COOH	C ₃ H ₇ OH	formate
00 g/11101				HCOOCH₃
	Boiling	118°C	97.8 °C	31.8 °C

·	point			
The molecular weight =		C₃H₁COOH Propanoic acid	C₄H ₉ OH butanol	CH ₃ COOCH ₃ Methyl acetate
74 g/mol	Boiling point	141 °C	118 °C	57 °C

Chemical properties:

1- <u>Hydrolysis</u> Alcohol and acid are produced from the hydrolysis of ester i.e. reverse to ester formation reaction.

$$R-C-OR + H_2O \longrightarrow R-C-OH + ROH$$

a- Hydrolysis may take place by the use of dilute mineral acids as a catalyst and is called (acid hydrolysis).

$$\begin{array}{c} O \\ H_3C\text{-}C\text{-}OC_2H_5 + H_2O \xrightarrow{H^+} & CH_3COOH + C_2H_5OH \\ \text{(A)} \end{array}$$

b- Hydrolysis of esters may also be carried out by heating with aqueous alkalis, to produce the alcohol and the salt of the acid. This is called alkaline- hydrolysis or saponification (Since soap is the sodium salt of high carboxylic acids).

$$\begin{array}{c} CH_{3}COOC_{2}H_{5} + NaOH \longrightarrow CH_{3}COONa + C_{2}H_{5}OH \\ \text{ethyl acetate} \end{array} \\ \text{(aq)} \qquad \text{sodium acetate} \qquad \text{(aq)} \end{array}$$

$$C_6H_5COOC_2H_5 + NaOH \rightarrow C_6H_5COONa + C_2H_5OH$$
 ethyl benzoate (A) (A) sodium benzoate (aq) (A)

2- Ammonolysis:

Esters react with ammonia to give acid amide and the alcohol.

$$\begin{array}{ccc} O & O \\ H_3C\text{-}C\text{-}OC_2H_5 + NH_3 & \longrightarrow & CH_3 - C\text{-}NH_2 + C_2H_5OH \\ \text{ethyl acetate}_{(\slashed{N})} & \text{(g)} & \text{acetamide}_{(\slashed{N})} \end{array}$$

$$\begin{array}{ccc} & & & & & O \\ C_6H_5-\overset{\parallel}{C}-OC_2H_5 + NH_3 & & & & C_6H_5-\overset{\parallel}{C}-NH_2 + C_2H_5OH \\ \text{ethyl bezoate}_{(\emph{N})} & & \text{benzamide} & & & (\emph{N}) \end{array}$$

Esters as Fats and oils:

Esters as polymers (Poly ester):

The most common poly ester is **Dacron** fibers which are prepared by the reaction between terphthalic acid and ethylene glycol (ester formation reaction).

Esters as medical drugs:

Organic esters are used in the manufacture of many drugs, the most common and simplest one is **aspirin** and oil of winter green (**Marookh oil**) which is used as local oil absorbed by the skin to decrease the pains of rheumatism.

The acid which is used in the manufacture of these two drugs is **salicylic** acid. Its molecule contains both the carboxylic and hydroxyl groups. It reacts as an acid or as an phenol as following equations.

Aspirin

Aspirin is the important drug which reduces the headache pains and temperature It also reduces the blood clotting and prevents the heart crises. The active substance in aspirin is salicylic acid however, the addition of **acetyl group** to the acid decreases its acidity effect and becomes tasteless.

Aspirin is hydrolysis in the body to produce salicylic acid and acetic acid.

The produced acids causes the excitation of stomach walls, and may cause stomach ulcer. Therefore doctors advice to crush the aspirin tablet as a powder before swallowing or taking it dissolved in water. There is a type of aspirin mixed with an alkaline substance like. aluminum hydroxide to neutralize the acidity produced.